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(21) International Application Number: PCT/GB98/03615 (22) International Filing Date: 8 December 1998 (08.12.98) (30) Priority Data: 9726008.7 10 December 1997 (10.12.97) GB (71) Applicant (for all designated States except US): THE SECRETARY OF STATE FOR DEFENCE (GB/GB); DERA, Ively Road, Farnborough, Hampshire GU14 0LX (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): GREEN, Kevin, John [GB/GB]; DERA Haslar, Gosport, Hants PO12 6AG (GB). WILSON, James, Charles [GB/GB]; DCS (R & T), MoD Main Building, Whitehall, London SW1A 2HB (GB). HOWE, Susan, Jennifer [GB/GB]; DERA Haslar, Gosport, Hants PO12 6AG (GB). BARNES, Philip, Nicholas [GB/GB]; DERA Haslar, Gosport, Hants PO12 6AG (GB). (74) Agent: BOWDERY, A., O.; D/TPR, Formalities Section (DERA), Poplar 2, MOD Abbey Wood #19, Bristol BS34 8JH (GB).			(81) Designated States: CN, GB, JP, KR, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.
(54) Title: ELECTROCHEMICAL CELL COMPRISING A LIQUID ORGANIC ELECTROLYTE WITH A CONDUCTIVE ADDITIVE			
(57) Abstract An electrochemical cell (1) comprises an anode (2), a solid cathode (3) and an electrolyte (4). The electrolyte comprises an electrochemically reactive conductive salt, an organic liquid phase comprising one or more organic compounds; and less than 0.25M of an ionically charged additive, distinct from the electrochemically reactive conductive salt. The additive comprises a conductive salt which in use is not electrochemically reactive and which has a nitrogen containing cation in a sufficient quantity that conductivity is improved and percentage material utilisation of the cathode is improved at increased discharge rates as compared with a cell using an electrolyte which does not contain the additive. An improvement of approximately 10 % in conductivity is achieved for a cell according to the invention using an electrolyte (c) with an additive.			

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ELECTROCHEMICAL CELL COMPRISING A LIQUID ORGANIC ELECTROLYTE WITH A CONDUCTIVE ADDITIVE

This invention relates to an electrochemical cell.

For the purpose of this description, electrochemical cells include primary
 5 rechargeable batteries and capacitors. An electrolyte in the electrochemical cell
 may conduct electricity through the movement of ions, charged species, towards an
 electrode having opposite electrical charge to the ions. Typically, the electrolytes
 consist of a salt, such as potassium chloride, dissolved in a solvent, which may be
 water (aqueous) or one or more organic compounds (non-aqueous). Alternatively,
 10 molten salts or ionic liquids, or room temperature molten salts (materials and
 mixtures which consist of an ionically bound liquid at ambient temperatures) may be
 used.

The conductivity of such electrolytes is dependent on several factors and
 several mathematical relationships have been developed. The *Nernst-Einstein*
 15 *Relationship* relates the ion diffusion coefficient and the ion conductivity. The
Stokes-Einstein Relationship relates the diffusion coefficient to the solution
 viscosity. Combining these relationships gives:

$$\lambda = \frac{kz^2 F^2}{6R\pi\eta a} \quad [1]$$

where λ is the conductivity, k is the Boltzman constant, z is the ionic charge, F is the
 20 Faraday Constant, R is the gas constant and η is the solution viscosity. The
 conductivity is also dependent on ion concentration:

$$\lambda = zc\mu F, \quad [2]$$

where λ is the conductivity, z the charge, c the ion concentration, and F is Faraday's
 Constant. Thus it can be seen that decreasing the viscosity and increasing the ion
 25 concentration is beneficial to the overall ionic conductivity.

An example of a primary battery is a lithium primary battery, especially those
 using a metal oxide or sulphide cathode and lithium foil anode. These batteries use
 electrolytes composed of one or more metal salts dissolved in a non-aqueous
 solvent, usually composed of more than one organic compound.

30 US-A 4537843 describes an example of a secondary battery having a polymeric
 electrode and an ammonium salt electrolyte. This type of electrolyte produces
 loose electrostatic bonding of positive and negative ions in solution at the surface of
 the electrodes when charged and the lithium salt is consumed by the cathode.

In accordance with the present invention, an electrochemical cell comprises an anode, a solid cathode and an electrolyte; wherein the electrolyte comprises an electrochemically reactive conductive salt, an organic liquid phase comprising one or more organic compounds; and less than 0.25M of an ionically charged additive, distinct from the electrochemically reactive conductive salt; the additive comprising a conductive salt, which in use is not electrochemically reactive and which has a cation containing one or more nitrogen atoms, in a sufficient quantity that conductivity is improved and percentage material utilisation of the cathode is maintained or improved at increased discharge rates as compared with a cell using an electrolyte which does not contain the additive.

The cell of the present invention has increased conductivity and decreased loss in material utilisation at the electrode compared with other cells such that the material utilisation observed at higher discharge rates is similar to that at low discharge rates. Electrochemical cells with the additive show improved discharge capacities and operating voltages compared to cells without the additive. Using an additive in the electrolyte which is not electrochemically reactive makes the system simpler and allows the cell chemistry to be predicted more easily. The effect of the additive is to maintain a background level of conductivity, which assists in mass transport of the principal conductive ions through the electrolyte solution, as can be seen in equation [2].

One method of determining the utilisation of the electrode material is to determine the number of Coulombs per gram of active material (C/g) achieved. This figure can then be compared to a theoretical maximum number of Coulombs that could possibly be passed knowing the amount of active material in the cathode, hence giving a percentage utilisation and the number of Coulombs passed per gram of material.

Preferably, the ionically charged additive comprises a quaternary aliphatic or cyclic aromatic ammonium salt. Where the reactive conductive salt comprises a quaternary ammonium salt, the non-reactive additive is a salt containing an aromatic nitrogen cation. Preferably, the ammonium salt comprises a 1 to 4 alkyl group substituted nitrogen containing cation, and an anion chosen from chlorides; perchlorates; phosphates, such as hexafluorophosphate; borates such as tetrafluoroborate; and sulphonates, such as trifluoromethanesulphonate, although other anion salts could be used.

Preferably the ionically charged additive comprises a salt with an aromatic nitrogen cation such as an imidazolium or pyridinium salt. Preferably, the additive

comprises a dialkyl substituted salt. More preferably, the alkyl substituents are independently selected from C₁ to C₄ alkyl groups. Alternatively, the salt is aryl substituted.

Preferably, the additive comprises an anion chosen from chlorides, perchlorates, phosphates, borates and sulphonates.

Preferably, the additive comprises chloride, hexafluorophosphate, tetrafluoroborate, trifluoromethanesulphonate and nitrate.

The maximum amount of additive is 0.25M, but preferably 0.05M of the ionically charged additive is used.

Preferably, the reactive conductive salt comprises an alkali or alkaline earth metal salt.

Preferably, the reactive alkali or alkaline earth metal salt comprises one of lithium, sodium, potassium, magnesium and calcium.

Preferably, the anions of the conductive salt comprise chlorides; perchlorates; phosphates, such as hexafluorophosphate; borates such as tetrafluoroborate; and sulphonates, such as trifluoromethanesulphonate, although other metal salts could be used.

Preferably, the organic solvent comprises one or more of cyclic carbonates and cyclic and linear ethers and polymers. For example, the organic liquid phase may be one or more of polyethyleneglycol, polyethylene oxide, propylene carbonate, ethylene carbonate, diethylcarbonate, dimethylcarbonate, ethylmethylcarbonate, tetrahydrofuran and dimethylglycoether, although other organic compounds may be used. For example polymer chains may be used to solvate the ionic species, sometimes organic solvents are used in addition to polymers. These have the effect of increasing the conductivity of polymeric systems.

Researchers have previously attempted to improve the performance of batteries using non-aqueous electrolytes by mixing in certain additives, either to improve the conductivity or stop deleterious side reactions. In the past researchers have added crown ethers, to improve lithium intercalation and carbon dioxide, to stabilise the lithium surface on recharge. Other compounds such as potassium hydroxide and potassium superoxide have been used to stabilise electrolytes and to improve the energy efficiency of the cell or battery. These function by reducing the chemical reactivity between the electrode material and the electrolyte.

The cells of the present invention are able to maintain the energy density of the battery at increasing discharge rates. At high rates of discharge (high currents) using conventional electrolytes, polarisation of ionic species and internal resistance

of the cell cause a loss of utilisation of available electrode material prior to the cut off voltage. The present invention decreases the loss in material utilisation at the electrode such that the material utilisation observed at higher discharge rates, is similar to that at low discharge rates.

5 Examples of electrochemical cells according to the present invention will now be described with reference to the accompanying drawing in which:

Figure 1 shows an example of an electrochemical cell according to the invention; and,

10 Figure 2 shows curves of cell potential against Coulombs/gram for five different additives and one example without additives.

Figure 1 shows a simple schematic of an electrochemical cell. The cell 1 comprises an anode 2 and a cathode 3 separated by a void which is filled with an electrolyte 4. For a battery the anodes and cathodes are different. For a supercapacitor the electrodes are essentially similar.

15 Figure 2 shows a plot of material utilisation (Coulombs/gram) against cell voltage. During discharge cell voltage decreases as duration continues. The time axis (material utilisation) increases with time. At a predetermined voltage the discharge is said to be over and the battery is termed to be exhausted.

Table One shows the ionic conductivity of a various electrolytes. The units for ionic conductivity are Simians per cm. Also given where determined is the % utilisation of the active cathode material. It is evident from the data that the additive improves the ionic conductivity of the base, or blank, electrolyte. In addition it is also evident that the % utilisation is also improved.

25 Cells using electrolytes based upon non-aqueous lithium ion conducting liquids were studied, although the lithium could be replaced by other alkali metal salts. The electrolytes were prepared in a conventional manner as follows. Dimethylethylene glycol (DME) (a.k.a dimethyglycolether) and ethylene carbonate (EC) were mixed together to form a single phase liquid. Sufficient lithium tetrafluoroborate (LiBF_4) was then dissolved in the liquid to give a one molar solution. Thereafter, sufficient material was added to give the required concentration to study the effect of the ionic additive. Other organic compounds which are suitable as solvents, include dialkyl solvents such as dimethylcarbonate and alkylene solvents such as propylene carbonate.

35 A number of tests were carried out using identical cathode and anodes and varying the electrolyte. In this example, the electrodes chosen were lithium as the anode material and manganese dioxide as the cathode material, though other

combinations are possible. The formation of such electrode films is well known in the literature.

The manganese dioxide was incorporated into an electrode by dissolving a suitable binder, in this case ethylene propylene diene monomer (EPDM), in cyclohexane. Sufficient manganese dioxide and carbon black (to give the electrode electronic conductivity) were then added to the monomer solution to form a slurry. The slurry was then coated onto aluminium foil. The solvent was allowed to dry, leaving a film of active material on the aluminium foil.

Lithium foil and the manganese dioxide containing electrode were cut to size and placed together separated by a plastic membrane (not shown). Then sufficient electrolyte was added to soak the electrodes and separator. The battery 1 was sealed in an airtight vessel, and discharged on a suitable piece of laboratory apparatus. The current density (amps per square centimetre) and the utilisation (amount of active material in the cathode reacted) were taken as the primary metrics to determine the effectiveness of the electrolyte additive.

During testing, the time from start, cell voltage and discharge current (held constant) were all monitored. The material efficiency was determined using the following equation:

material utilisation = (discharge current*discharge time)/(mass of active material).

In this way small variations in cathode weights could be accounted for. For each time increment the cell voltage and material utilisation were then plotted. The resultant graphs showed that the additive generally gave a higher cell voltage on discharge and an increased material utilisation.

The results are illustrated in Fig. 2. Two blank solutions (no additive) were studied for comparative purposes. One was 1M LiBF₄ (f) in DME:EC (1:1 by weight) and the other was 1.05M LiBF₄ (g). The ionic materials studied were based upon the imidazolium cation, and several salts were studied in which the anion of the material varied. These were 3-ethyl-1-methyl imidazolium hexafluorophosphate (a); 3-ethyl-1-methyl imidazolium tetrafluoroborate (b); 3-ethyl-1-methyl imidazolium chloride (c); 3-ethyl-1-methyl imidazolium trifluoromethane sulphonate (d); and 3-ethyl-1-methyl imidazolium nitrate (e). Although other suitable materials exist, the examples illustrate the benefits of using these additives in producing higher than expected conductivity. The quantity of additive used was 0.05M in each case, however, up to 0.25M may be added to achieve the desired effect. The conductivity

and percentage utilisation (at a high current rate of 10 mA/cm²) is summarised in table 1 below.

The cation could be any nitrogen containing cation e.g. other quarternary nitrogen heterocycles, such as pyridinium. Other examples of electrochemical cells according to the invention are rechargeable batteries which benefit from the increase in utilisation rate, and electrochemical or double layer capacitors and electrochromic windows where the increased conductivity is particularly useful.

Additive / cation (0.05M)	Conductivity / S cm ⁻¹	% Utilisation
[blank]	0.0116	62
imidazolium salts		
chloride	0.0120	67
hexafluorophosphate	0.0123	72
tetrafluoroborate	0.0124	71
trifluoromethanesulphonate	0.0121	69
nitrate	0.0125	66
tetraalkylammonium salts		
hexafluorophosphate	0.0119	-
tetrafluoroborate	0.0122	-

Table 1: Effect of additive on electrolyte

CLAIMS

1. An electrochemical cell, the cell comprising an anode, a solid cathode and an electrolyte; wherein the electrolyte comprises an electrochemically reactive
5 conductive salt, an organic liquid phase comprising one or more organic compounds; and less than 0.25M of an ionically charged additive, distinct from the electrochemically reactive conductive salt; the additive comprising a conductive salt, which in use is not electrochemically reactive and which has a cation containing one or more nitrogen atoms, in a sufficient quantity that conductivity is improved and
10 percentage material utilisation of the cathode is maintained or improved at increased discharge rates as compared with a cell using an electrolyte which does not contain the additive.
2. An electrochemical cell according to claim 1, wherein the ionically charged
15 additive comprises a quarternary aliphatic or cyclic aromatic ammonium salt.
3. An electrochemical cell according to claim 1 or claim 2, wherein the reactive conductive salt comprises a quaternary ammonium salt; and wherein the non-reactive additive is a salt containing an aromatic nitrogen cation.
20
4. An electrochemical cell according to claim 3, wherein the ammonium salt comprises a 1 to 4 alkyl group substituted nitrogen containing cation.
5. An electrochemical cell according to at least claim 3, wherein the
25 quarternary ammonium salt comprises an anion chosen from chlorides, perchlorates, phosphates, borates and sulphonates.
6. An electrochemical cell according to any preceding claim, wherein the ionically charged additive comprises a salt with an aromatic nitrogen cation such as
30 an imidazolium or pyridinium salt.
7. An electrochemical cell according to claim 6, wherein the ionically charged additive comprises a dialkyl substituted salt.
8. An electrochemical cell according to claim 7, wherein the alkyl substituents
35 are independently selected from C₁ to C₄ alkyl groups.

9. An electrochemical cell according to any preceding claim, wherein the additive comprises an anion chosen from chlorides, perchlorates, phosphates, borates and sulphonates.
- 5 10. An electrochemical cell according to any preceding claim, wherein 0.05M of additive is provided.
- 10 11. An electrochemical cell according to claim 1 or claim 2, wherein the reactive conductive salt comprises an alkali or alkaline earth metal salt.
12. An electrochemical cell according to claim 11, wherein the alkali or alkaline earth metal comprises one of lithium, sodium, potassium, magnesium and calcium.
- 15 13. An electrochemical cell according to any preceding claim, wherein the anion of the conductive salt is one of chloride, perchlorate, phosphate, borate and sulphonate.
- 20 14. An electrochemical cell according to any preceding claim, wherein the organic solvent comprises one or more of a cyclic carbonate, cyclic and linear ethers and polymers.
- 25 15. An electrochemical cell according to any preceding claim, wherein the organic liquid phase comprises one or more of polyethyleneglycol, polyethylene oxide, propylene carbonate, ethylene carbonate, diethylcarbonate, dimethylcarbonate, ethylmethylcarbonate, tetrahydrofuran and dimethylglycoether.

Fig.1.

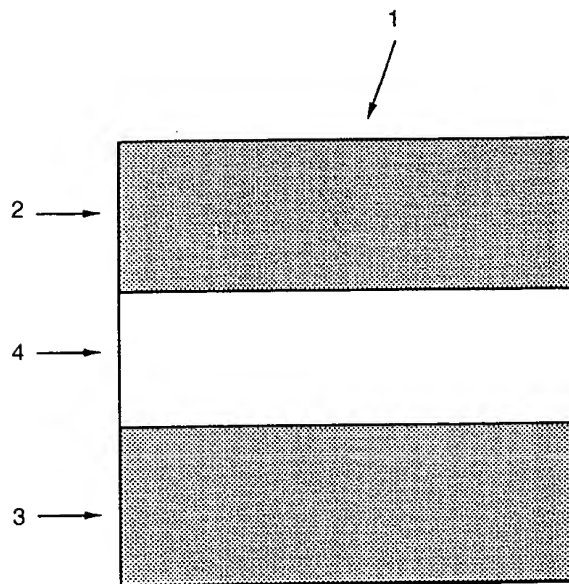
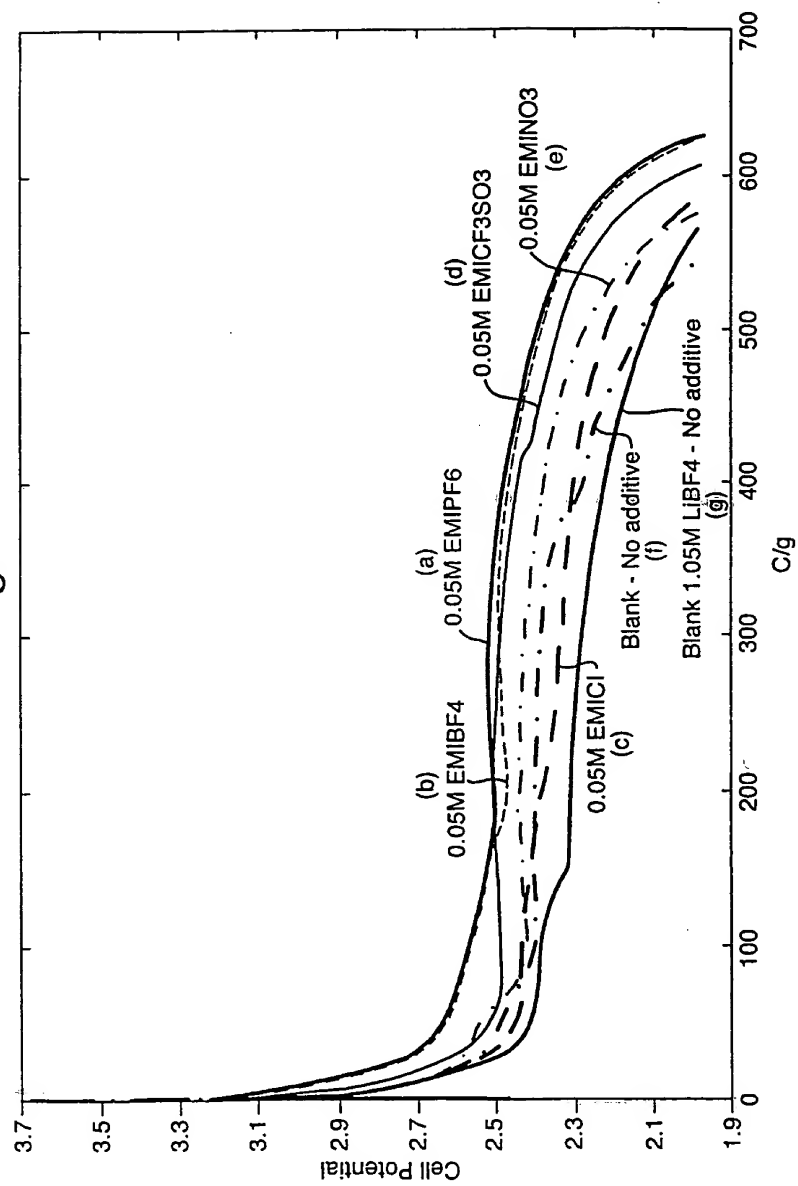


Fig.2.



INTERNATIONAL SEARCH REPORT

national Application No
PCT/GB 98/03615A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01M6/16 H01M10/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01M

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 704 099 A (CENTRE NAT ETD SPATIALES) 21 October 1994 see page 3, line 22 - page 6, line 4 see claims ---	1-15
X	HIRAI T ET AL: "EFFECT OF ADDITIVES ON LITHIUM CYCLING EFFICIENCY" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 141, no. 9, September 1994, pages 2300-2305, XP000469418 see the whole document ---	1-5,9-15
A	US 4 526 846 A (KEARNEY SUSAN D ET AL) 2 July 1985 see column 1, line 58 - column 2, line 41 see claim 3 --- -/--	1-15

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 132 837 A (SOFFER ABRAHAM) 2 January 1979 see the whole document ----	1-15
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 139 (E-738), 6 April 1989 & JP 63 301467 A (MATSUSHITA ELECTRIC IND CO LTD), 8 December 1988 see abstract ----	1-15
A	EP 0 785 586 A (FUJI PHOTO FILM CO LTD) 23 July 1997 see page 4, line 1 - page 7, line 44 -----	1-15

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/03615

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